Overtone spectra and intensities of tetrahedral molecules in boson-realization models

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The stretching and bending vibrational spectrum and the intensities of infrared transitions in a tetrahedral molecule are studied in two boson-realization models, where the interactions between stretching and bending vibrations are described by a quadratic cross term and by Fermi resonance terms, called harmonically coupled and Fermi resonance boson-realization model, respectively. The later is a development of our recent model. As an example, the two models are applied to the overtone spectrum and the intensities of silicon tetrafluorde. Those models provide fits to the published experimental vibrational eigenvalues with standard deviations 1.956 cm^{-1} and 0.908 cm^{-1}, respectively. The intensities of infrared transitions of its complete vibrations are calculated in the two models, and results show a good agreement with the observed data.

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I. INTRODUCTION

In recent years, algebraic methods have been introduced for a description of rotation-vibrational spectra of molecules. A U(4) algebraic model [1] was successfully used to explain the rotation-vibrational states of diatomic molecules. This model was developed for studying small molecules by introducing a U(4) algebra for each bond [2,3]. It was also suggested to use a U($k + 1$) model [4] for the $k = 3m - 3$ rotational and vibrational degrees of freedom of m-atomic molecules. Those two models have an advantage that they can treat rotations and vibrations simultaneously, but they are quite complex for larger molecules. A U(n) algebraic approach [5] was also used for a treatment of $n - 1$ stretching vibrational degrees of freedom in polyatomic molecules. Iachello and Oss presented a SU(2) algebraic model based on isomorphism between the one-dimensional Morse oscillator and the SU(2) algebra, which was particularly well suited for dealing with the stretching vibrations of polyatomic molecules such as the octahedral and benzene-like systems [6]. The U(4) and SU(2) algebraic models were even modified by the corresponding quantum algebraic ones [7,8] for diatomic molecules.

Incorporating the bending modes in algebraic models for large molecules was not achieved until 1993, when Iachello and Oss proposed a U(2) algebraic model for describing Pöschl-Teller oscillator that was well suitable for bending vibrations [9]. They extended this method to treat coupled bending modes [10]. Frank *et al.* presented a symmetry-adapted algebraic model [11-13], which described the stretching and bending vibrations in terms of U(2) algebra and made a clear connection between the algebraic approaches and the traditional methods in the configuration space. In a different way, by making use of the bosonic operators for describing vibrations, Ma *et al.* have recently introduced an algebraic model of boson realization [14] for the complete vibrational modes, and obtained the satisfactory results for some molecules [15,16].

In this paper we will further investigate both the complete vibrations and the intensities of infrared transitions in a tetrahedral molecule in two boson-realization models. The first model is the model that we proposed recently [14], where the interactions between the stretch and the bend are harmonically coupled. Let us refer this model as a harmonically coupled boson-realization model (HCBM). The second model is called Fermi resonance boson-realization model (FRBM), where the interactions between two kinds of vibrations are described by Fermi resonances. As an example of their applications, we study the vibrational spectrum of silicon tetrafluorde SiF_4 in two models. HCBM with seven parameters and FRBM with ten parameters provide fits to the observed values with the standard deviation 1.956 cm^{-1} and 0.908 cm^{-1}, respectively. Furthermore, we propose another FRBM with only seven parameters, where the standard deviation is still about half of that in HCBM with the same number of parameters. It shows that FRBM is more suitable for highly excited states in this molecule. In addition, intensities of infrared transitions of both the stretching and the bending vibrational spectrum in this molecule are calculated in the two models, and indicate a good agreement with the experimental values.

The organization of this paper is as follows. Sec. II is devoted to construct the symmetrized bases and identify the spurious states. In Sec. III the vibrational Hamiltonian in the two models are

introduced in terms of ten sets of boson operators and applied to the vibrational spectrum of silicon tetrafluoride SiF_4. Its intensities of infrared transitions in the two models are presented in Sec. IV. Conclusion is made in Sec. V.

II. SYMMETRIZED BASES AND SPURIOUS STATES

In calculating spectra of polyatomic molecules one needs to construct a basis in which the Hamiltonian matrix is a block matrix. The symmetry adapted bases are widely used for this purpose. Halonen and Child [17] gave symmetrized local mode basis functions for stretching vibrations of symmetry molecules by a combination of promotion operators and Schmidt orthogonalization. Frank *et al.* [11-13] first constructed the symmetrized bases by projecting the one-phonon local functions, and then obtained the higher-phonon functions from the one-phonon symmetrized states by the Clebsch-Gordan coefficients. This method is quite complex when describing vibrations of large molecules and for high overtones. In this case, the symmetry adapted bases can be achieved by a new technique for constructing representations of the molecular symmetry point groups, that was recently called symmetrized boson representations [18]. This new technique has merits that the basis vectors of those representations have a clear physical picture, and that their combinations are much simpler and general for multiple-phonon states. In this way we constructed the symmetrized bases for a tetrahedral molecule [14]. We hereby outline them for completeness.

For a tetrahedral molecule XY_4 there are four stretching oscillators and six bending oscillators. As in our previous paper [14], let the atom X locate at the center O of the tetrahedron, and the four atoms Y at its vertices A, B, C, and D. The coordinate axes x, y, and z point from O to the centers of edges AC, AD, and AB, respectively. The four stretching oscillators OA, OB, OC, and OD, which are enumerated one to four, are described by four equivalent bosonic operators $a_j^\dagger$ (a_j), $1 \le j \le 4$. The six bending oscillators $\angle$ AOB, $\angle$ AOC, $\angle$ AOD, $\angle$ COD, $\angle$ DOB, and $\angle$ BOC, enumerated by five to ten, are described by six equivalent bosonic operators $a_\mu^\dagger$ (a_μ), $5 \le \mu \le 10$. Those ten sets of bosonic operators satisfy the well known algebraic relations. Hereafter, the indexes j, μ, and α run from 1 to 4, 5 to 10, and 1 to 10, respectively, and n_α denotes the phonon number on the αth oscillator, and n_s and n_b the total phonon numbers on stretching and bending oscillators, respectively.

From the standard method of group theory, it is easy to reduce the regular representation of the point group T_d. Applying those combinations of group elements, that belong to irreducible representations of T_d, to the states $|n_1 n_2 n_3 n_4\rangle$ for pure stretching vibrations and the states $|n_5 n_6 n_7 n_8 n_9 n_{10}\rangle$ for pure bending vibrations, respectively, we generally obtain the symmetry adapted bases for the states with any phonon number. Then, the product of two bases can be combined into irreducible bases by the Clebsch-Gordan coefficients of T_d, denoted as $|n\rangle \equiv |n_1 n_2 n_3 n_4 n_5 n_6 n_7 n_8 n_9 n_{10}\rangle$.

For the fundamental bending vibrations ($n_b = 1$) there are six states belonging to three irreducible representation: A_1, E, and F_2. As is well known [19], there are only five degrees of freedom for the bending vibrations ($E \oplus F_2$), because there is a constraint between the six angles. The state belonging to the representation A_1 is called the fundamental spurious state:

$$\psi(A_1, 100000) = 6^{-1/2} \sum_{\mu=5}^{10} |1_\mu\rangle, \tag{2.1}$$

where $|1_\mu\rangle$ denotes the first excited state of the μth oscillator. This state introduces a spurious degree of freedom that should be removed.

Some methods for removing the spurious states were recently introduced. Iachello and Oss [9] placed the spurious states at the energies ≥ 10 times the energies of the physical states by projection operators. This method of removal is exact for harmonic bending vibrations and acquires a small error for anharmonic ones. Instead, Lemus and Frank [13] directly eliminated the spurious states from both the space and the Hamiltonian. They demanded the matrix elements of the Hamiltonian related to the fundamental spurious state $\psi(A_1, 100000)$ vanishing. However, it is impossible to demand all the matrix elements of the Hamiltonian that related to the spurious states vanishing. In Ref. [14] a criterion for identifying the spurious states was introduced: a state is a spurious state if it contains $\psi(A_1, 100000)$ as a factor. In addition, the bases of the physical states are chosen to be orthogonal with each other and with all the spurious states. In next section we will use this criterion to remove the spurious states from Hamiltonian and the symmetrized bases.

III. HAMILTONIAN

Studies of the vibrations in a tetrahedral molecule already exist in the literature. Its excited stretching vibrational states were explained in the local mode model [17] and a U(5) algebraic model [5]. A U(2) algebraic approach [13] was proposed for both stretching and bending modes, where the interactions between the stretch and the bend were neglected. In our previous papers [14,15] we studied the vibrational spectrum of methane in boson-realization model in terms of bosonic operators and q-deformed harmonic oscillators, however, intensities of infrared transitions were not involved. We will further research both the vibrational energy levels and intensities of a tetrahedral molecules in the two different models, and apply it to the spectrum of SiF_4.

A. HARMONICALLY COUPLED BOSON-REALIZATION MODEL

First of all, we outline the boson-realization model that we recently introduced in [14], where the interactions between the stretch and the bend are described by a quadratic cross term. We here call it as the harmonically coupled boson-realization model (HCBM). Then, we calculate the energy levels of SiF_4 in HCBM.

For simplicity we assume that all oscillators are the Morse ones with two parameters ω and x, so that the energies of those oscillators can be expressed in the operator form:

$$E_s(n_j) = n_j \left\{ \omega_s - x_s(n_j + 1) \right\}, \quad 1 \leq j \leq 4,$$

$$E_b(n_\mu) = n_\mu \left\{ \omega_b - x_b(n_\mu + 1) \right\}, \quad 5 \leq \mu \leq 10, \tag{3.1}$$

where the null energy has been removed.

The vibrational Hamiltonian H of the molecule XY_4 is T_d invariant and is assumed to preserve the total number of quanta $n = n_s + n_b$. Since $a_j^\dagger$ (a_j) and $a_\mu^\dagger$ (a_μ) are the tensor operators belonging to $A_1 \oplus F_2$ and $A_1 \oplus E \oplus F_2$, respectively, and $\sum a_\mu$ (or $\sum a_\mu^\dagger$) only annihilates (or creates) the spurious states, we can express Hamiltonian H as the T_d invariant combinations of the products of one creation operator and one annihilation operator [15]:

$$H = \sum_{j=1}^{4} E_s(a_j^\dagger a_j) + \sum_{\mu=5}^{10} E_b(a_\mu^\dagger a_\mu) + \lambda_s \sum_{i \neq j} a_i^\dagger a_j$$

$$+ \ \lambda_b \sum_{\mu=5}^{7} \left(a_\mu^\dagger a_{\mu+3} + \text{H.c.} \right) \ + \ \lambda_{sb} \left\{ a_1^\dagger \sum_{\mu=5}^{7} (a_\mu - a_{\mu+3}) \right.$$

$$+ \ a_2^\dagger \left(a_5 - \sum_{\mu=6}^{8} a_\mu + a_9 + a_{10} \right) \quad + a_3^\dagger \sum_{\mu=3}^{5} (a_{2\mu} - a_{2\mu-1})$$

$$+ \ a_4^\dagger \left(-a_5 - a_6 + \sum_{\mu=7}^{9} a_\mu - a_{10} \right) + \text{H.c.} \left. \right\}, \tag{3.2}$$

where λ_s and λ_b are the coupling strength among stretching modes and bending ones, respectively. The term with λ_{sb} describes the interaction between stretching and bending vibrations, which was neglected in Ref. [13] for simplicity. The Hamiltonian H contains seven parameters: ω_s, x_s, ω_b, x_b, λ_s, λ_b, and λ_{sb}.

Following the criterion in Sec. II for eliminating the spurious states from the bases and straight calculating, we find that for $n = 1$ and representation A_1, there is one physical state, for $n = 1$ and E there is only one set of physical states, for n=1 and F_2 there are two sets of physical states, for n=2 and F_2 there are seven sets of physical states, and for n=3 and F_2, there are 25 sets of physical states, and for n=4 and F_2, there are 69 sets of physical states. Those combinations for $n = 1, 2$ were given in Ref. [14], and others can be obtained from us upon request.

In those bases of the physical states the Hamiltonian becomes a symmetric block matrix. The energies of physical states can be calculated provided that the parameters of the Hamiltonian are known. A least-square fitting is adopted to get the parameters from the observed data. The observed energy levels from Ref. [20] and the corresponding calculated values are given in Table I, where the standard deviation (SD) in this fit (Fit A) is 1.956 cm^{-1}. The seven parameters obtained are given in Table II. In terms of those parameters one can calculate the other energy levels. Since the infrared experimental dipole transitions energies correspond to F_2, we hereby only list the calculation results for other F_2 states in Table III.

Table I

Table II

Table III

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From Table II we see that the ratio $|w_s/x_s|$ of the stretching modes is larger than that of the bending ones. It means that, contrary to the case in methane [14], the anharmonicity of bending modes in SiF_4 is larger than that of the stretching ones. At least, the anharmonicity of the vibrations depends upon the molecules discussed.

B. FERMI RESONANCE BOSON-REALIZATION MODEL

With the development and refinement of experimental techniques in high-resolution spectroscopy, measurements of high excited vibrational spectra for molecules become available [21]. One of important characters in highly excited states is appearance of anharmonic resonances. Fermi resonance (FR), one of these resonances, is taken into account for description of molecular vibrations. In the normal mode model, FR terms were treated as perturbative corrections [22], while they were described by the nondiagonal matrix elements of Majorana operators in U(4) algebraic model [23]. Recently, simple Fermi resonance-local mode models for bent triatomic molecules [24] and pyramidal XY_3 molecules [25] have been constructed by Halonen *et al.*, where FR terms are expressed in terms of curvilinear internal valence coordinates. In addition, FR can be of central importance for intramolecular vibrational redistribution and kinetics [26]. Therefore, it is necessary for us to consider FR in the boson-realization model. We present an extended model, called Fermi resonance boson-realization model (FRBM), and it is pleasure to see that FRBM provides smaller standard deviation than HCBM in the energy level fits of SiF$_4$.

We introduce another vibrational Hamiltonian for a tetrahedral molecule, where the interactions between stretching and bending vibrations are described by the T_d symmetric FR terms that couple one creation (or, respectively, annihilation) operator of stretching vibrations with two annihilation (or, respectively, creation) operators of bending ones. Although $a_\mu a_\nu$ belongs to $3A_1 \oplus 3E \oplus 3F_2 \oplus F_1$, we find only four independent T_d invariant combinations related to physical states:

i) $A_1 \otimes (E \otimes E)_{A_1}$,

$$H_1 = \left(\sum_{j=1}^{4} a_j^\dagger \right) \left(\sum_{\mu=5}^{10} a_\mu^2 - \sum_{\mu<\nu=6}^{10} a_\mu a_\nu + 3 \sum_{\mu=5}^{7} a_\mu a_{\mu+3} \right) + \text{H.c.}, \tag{3.3}$$

ii) $A_1 \otimes (F_2 \otimes F_2)_{A_1}$,

$$H_2 = \left(\sum_{j=1}^{4} a_j^\dagger \right) \left(\sum_{\mu=5}^{10} a_\mu^2 - 2 \sum_{\mu=5}^{7} a_\mu a_{\mu+3} \right) + H.c., \tag{3.4}$$

iii) $F_2 \otimes (E \otimes F_2)_{F_2}$,

$$H_3 = \left(a_1^\dagger - a_2^\dagger + a_3^\dagger - a_4^\dagger \right) (a_6 - a_9) \left(3a_6 + 3a_9 - \sum_{\mu=5}^{10} a_\mu \right)$$

$$+ \left(a_1^\dagger - a_2^\dagger - a_3^\dagger + a_4^\dagger \right) (a_7 - a_{10}) \left(3a_7 + 3a_{10} - \sum_{\mu=5}^{10} a_\mu \right)$$

$$+ \left(a_1^\dagger + a_2^\dagger - a_3^\dagger - a_4^\dagger\right)(a_5 - a_8)\left(3a_5 + 3a_8 - \sum_{\mu=5}^{10} a_\mu\right) + H.c., \quad (3.5)$$

iv) $F_2 \otimes (F_2 \otimes F_2)_{F_2}$,

$$H_4 = \left(a_1^\dagger - a_2^\dagger + a_3^\dagger - a_4^\dagger\right)(a_5 - a_8)(a_7 - a_{10})$$

$$+ \left(a_1^\dagger - a_2^\dagger - a_3^\dagger + a_4^\dagger\right)(a_5 - a_8)(a_6 - a_9)$$

$$+ \left(a_1^\dagger + a_2^\dagger - a_3^\dagger - a_4^\dagger\right)(a_6 - a_9)(a_7 - a_{10}) + H.c.. \quad (3.6)$$

Now, we obtain the following T_d invariant Hamiltonian with ten parameters:

$$H = \sum_{j=1}^{4} E_s(a_j^\dagger a_j) + \sum_{\mu=5}^{10} E_b(a_\mu^\dagger a_\mu) + \lambda_s \sum_{i\neq j=5}^{10} a_i^\dagger a_j + \lambda_b \sum_{\mu=5}^{7} \left(a_\mu^\dagger a_{\mu+3} + a_{\mu+3}^\dagger a_\mu\right)$$

$$+ \lambda_{f1} H_1 + \lambda_{f2} H_2 + \lambda_{f3} H_3 + \lambda_{f4} H_4, \quad (3.7)$$

where the Hamiltonian preserve the quantum number $N = 2n_s + n_b$.

The symmetrized bases are also used in the calculation. Using the same method for removing the spurious states as described in Sec. II, we find that there are 1 set of states with $N = 1$ for representation E (no spurious state), and 3 states with N=2 for A_1 (removing 1 spurious state), and for the representation F_2 there are 1 set of states with $N = 1$ (no spurious state), 3 sets of states with $N = 2$ (removing 1 set of spurious state), 8 sets of states with $N = 3$ (removing 4 sets of spurious states), 20 sets of states with $N = 4$ (removing 12 sets of spurious states), 43 sets of states with $N = 5$ (removing 32 sets of spurious states), and 90 sets of states with $N = 6$ (removing 75 sets of spurious states). The physical states and the Hamiltonian matrices in those physical states are evaluated with the help of the computer algebra program MATHEMATICA [27].

For comparison, we also list the ten parameters determined by fitting the same 16 experimental data (Fit B) in Table II and the calculated results in Table I, respectively. The standard deviation in this fit is 0.908 cm^{-1}. Other calculation results for the spectrum only for F_2 are given in Table IV.

$$\boxed{\text{Table IV}}$$

From Table II we see that the parameters λ_{f2}, λ_{f3} and λ_{f4} are quite small. It provides us a possibility to set those three parameters vanishing. In this way another fitting (Fit C) is obtained with the standard deviation 0.989 cm^{-1}, where it contains the same number of parameters as in Fit A. This standard deviation is about one half of that in Fit A. The seven parameters and the calculated values obtained in Fit C are given in the corresponding tables.

It is interesting to compare the obtained parameters in the three fits. From Table II, when FR terms (Fit B) is replaced with the harmonical coupling (Fit A) between the stretch and the bend, the biggest change of the parameters is that of the anharmonic constant x_s in Morse oscillator of the stretch, while parameter λ_b for the interactions between the bending vibrations gets the least change.

When the three small FR parameters are set to be zero (Fit C), other parameters change very little in comparison with those in Fit B. Fit C provides less standard deviation than Fit A with the same number of parameters. To our knowledge, it may be the model with the least parameters that well fits the observed vibrational spectrum of SiF_4. In principle, the physical meaning of those obtained parameters can be explained in terms of internal coordinate.

It is worth mentioning that McDowell *et al.* [20] described the same vibrational spectrum of SiF_4 by the normal mode model with more parameters. This model provides the normal mode labels for small amplitude polyatomic molecular vibrational spectra. However, it becomes less appropriate at higher levels of vibrational excitation. In particular, the assignment of sets of normal mode quantum numbers to give spectral absorption features becomes inherently ambiguous [28]. This model does not provide explicitly wave functions so that some physical properties such as transition intensities are hard to be calculated.

IV. INTENSITIES OF INFRARED TRANSITION

Having completed calculations for the vibrational energy levels of SiF_4, we are now able to compute the intensities of infrared transition for all active modes. This information can be used to check the assignments and in the study of intramolecular energy relaxation in SiF_4. For stretching vibrations of tetrahedral molecules, Leroy *et al.* [29] recently constructed an electric dipole moment operator through unitary algebra and point group symmetry. However, their dipole function is not feasible for treating other vibrational modes. Intensities of infrared and Raman transition of stretching modes in octahedral molecules were analyzed by Chen *et al.* [30] in terms of U(2) algebra. In this section, intensities of infrared transition for all active modes of SiF_4 will be computed in the two approaches presented in Sec. III.

The absolute absorption intensities from state n' to n in the infrared active mode F_2 are given by

$$I_{nn'} = \nu_{nn'} P_{nn'},$$

$$P_{nn'} = |\langle n|\hat{T}_x|n'\rangle|^2 + |\langle n|\hat{T}_y|n'\rangle|^2 + |\langle n|\hat{T}_z|n'\rangle|^2, \tag{4.1}$$

where $\nu_{nn'}$ is the frequency of the observed transition, and $\hat{T}_x$, $\hat{T}_y$, and $\hat{T}_z$ correspond to the three components of the infrared transition operator $\hat{T}$. All other constants are absorbed in the normalization of the operator $\hat{T}$. The three components of $\hat{T}$ are

$$\hat{T}_x = \gamma_s \ (\hat{t}_1 - \hat{t}_2 + \hat{t}_3 - \hat{t}_4) \ + \ \gamma_b \ (\hat{t}_6 - \hat{t}_9) \ + \ \gamma_{sb} \ (\hat{t}_1 + \hat{t}_2 + \hat{t}_3 + \hat{t}_4)(\hat{t}_6 - \hat{t}_9),$$

$$\hat{T}_y = \gamma_s \ (\hat{t}_1 - \hat{t}_2 - \hat{t}_3 + \hat{t}_4) \ + \ \gamma_b \ (\hat{t}_7 - \hat{t}_{10}) \ + \ \gamma_{sb} \ (\hat{t}_1 + \hat{t}_2 + \hat{t}_3 + \hat{t}_4)(\hat{t}_7 - \hat{t}_{10}),$$

$$\hat{T}_z = \gamma_s \ (\hat{t}_1 + \hat{t}_2 - \hat{t}_3 - \hat{t}_4) \ + \ \gamma_b \ (\hat{t}_5 - \hat{t}_8) \ + \ \gamma_{sb} \ (\hat{t}_1 + \hat{t}_2 + \hat{t}_3 + \hat{t}_4)(\hat{t}_5 - \hat{t}_8), \tag{4.2}$$

where γ_s, γ_b, and γ_{sb} are parameters, and $\hat{t}_\alpha$ is the local operator on the αth bond. The term with γ_{sb} is the higher order contribution of $\hat{T}$, which is necessary for describing both the stretching and

the bending active modes in SiF_4. Following [9] we take the matrix elements of $\hat{t}_\alpha$ as follows:

$$\langle n|\hat{t}_j|n'\rangle \;=\; exp(-\eta_j|n_j - n'_j|), \quad 1 \le j \le 4,$$

$$\langle n|\hat{t}_\mu|n'\rangle \;=\; exp(-\eta_\mu|n_\mu - n'_\mu|), \quad 5 \le \mu \le 10, \tag{4.3}$$

where the coefficients η_j should be equal for the equivalent bonds $\eta_j \equiv \eta_s$, and $\eta_\mu \equiv \eta_b$.

Since calculations are done in the symmetrized bases it is sufficient to consider only the z component, $\hat{T}_z$. All others can be obtained by making use of the Wigner-Eckart theorem. The relative intensities calculated in Fit A and Fit B are given in Table I, where they are compared with experiment. The corresponding parameters and the standard deviations (SD) are listed in Table V. In the two fits, the obtained parameters in the operator of infrared transition have a little difference, but the calculated intensities for a few energy levels are quite different. This is owing to the different wave functions and the same transition operator in the two models.

$$\boxed{\text{Table V}}$$

In Table I most of calculated intensities for the two models are in good agreement with the experimental values, but a few are not. Those differences may come from two sources. The observed intensities are only approximately accurate [20], and the other higher order contributions to the operator $\hat{T}$ are neglected. The more accurate experimental data are needed to improve the models.

In order to complete the spectroscopic study of vibrational overtone of SiF_4, we should also calculate the intensities of Raman transition in the two models. Unfortunately, We have to postpone this calculation due to lack of the observed values.

V. CONCLUSION

For studying the stretching and bending spectrum of a tetrahedral molecule, we have presented a harmonically coupled boson-realization model (HCBM) and a Fermi resonance boson-realization model (FRBM), where the coupling between the stretch and the bend is described by a quadratic cross term and by Fermi resonance terms, respectively. The two models have been applied to the complete vibrations of silicon tetrafluoride SiF_4. HCBM with seven parameters and FRBM with ten parameters provide fits to the published experimental vibrational eigenvalues with standard deviations 1.956 cm^{-1} and 0.908 cm^{-1}, respectively. This is based on our new method for constructing symmetrized bases [14] and for removing both the spurious states in the wavefunction space and the spurious components in Hamiltonian [15]. This method is particularly useful for highly excited states in large molecules. In another FRBM, we decrease the number of parameters and obtain the standard deviation 0.989 cm^{-1} that is about half of that in HCBM with the same number of parameters. To our knowledge, FRBM may be the model for a good description of vibrational spectrum of SiF_4 with the least parameters. We believe that FRBM will be better suitable for describing highly excited vibrations in molecules.

The intensities of infrared transitions of the complete vibrations in this molecule have been calculated in those two models. The model transition operator with five parameters well reproduces the

observed data. The more satisfactory results can be obtained if more accurate experimental values are available.

Finally, we remark that our models can be extended in several ways. The Fermi resonances may be taken into account as perturbative terms in HCBM, or the harmonically coupled term appears in FRBM as a perturbative one. Other anharmonic resonances such as Darling-Dennison resonances can be included in the models by adding higher-order terms of bosonic operators [16]. The rotational degrees of freedom can be incorporated by coupling the vibrational wave functions to rotational states carrying the appropriate point symmetries [31]. Our algebraic Hamiltonian can be written down in the coset space representation to study the dynamics of stationary eigenstates and inter-mode energy transfer [32]. Work on those subjects is in progress.

ACKNOWLEDGMENTS

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Table I. Observed and calculated energy levels and relative intensities for SiF$_4$

	Obs.[20]			Fit A			Fit B		Fit C
Γ	E (cm^{-1})	Intensity	n	E (cm^{-1})	Intensity	N	E (cm^{-1})	Intensity	E(cm^{-1})
E	264.2		1	262.593		1	262.616		263.043
F_2	388.4448	500	1	387.029	499.966	1	388.112	500.086	387.552
F_2	776.3	0.9	2	776.028	0.968	2	776.196	0.413	775.104
A_1	800.8		1	803.333		2	800.195		799.847
F_2	1031.3968	5000	1	1031.338	4999.989	2	1030.951	5000.031	1030.818
E	1064.2		2	1065.926		3	1064.486		1064.411
F_2	1164.2	1.4	3	1164.348	4×10^{-4}	3	1164.939	4.117	1165.115
F_2	1189.7	40	2	1190.361	40.073	3	1190.236	39.631	1190.531
F_2	1294.05	2.4	2	1293.938	1×10^{-4}	3	1294.308	0.009	1293.861
F_2	1418.75	0.1	2	1418.367	2×10^{-4}	3	1418.989	1×10^{-5}	1418.370
F_2	1804.5	0.7	3	1805.405	2×10^{-6}	4	1804.941	0.002	1805.922
F_2	1828.17	7	2	1828.098	3.820	4	1828.219	3.909	1828.083
F_2	2059.1	1.2	2	2056.461	3.653	4	2059.016	4.193	2059.098
F_2	2602.55	0.007	4	2602.163	2×10^{-9}	6	2601.910	2×10^{-6}	2602.273
F_2	2623.8	0.015	3	2621.531	0.002	6	2624.028	0.007	2624.067
F_2	3068.5	0.015	3	3071.082	0.004	6	3068.276	0.005	3068.251

Table II. Parameters in the Hamiltonian obtained by the least square fitting $\left(cm^{-1}\right)$

	stretching			bending			interactions				SD
	ω_s	x_s	λ_s	ω_b	x_b	λ_b	λ_{sb} (λ_{fk}, $k=1,4$)				
Fit A	987.106	6.395	-56.995	135.205	-94.810	-62.232	1.486				1.956
Fit B	978.898	2.930	-57.661	133.656	-95.854	-62.748	1.274	0.431	0.772	0.635	0.908
Fit C	978.043	2.567	-57.909	132.979	-96.159	-62.255	1.167*				0.989

* $\lambda_{f2} = \lambda_{f3} = \lambda_{f4} = 0$.

Table III. The calculated energy levels in Fit A for other F_2 states without observed data (in cm^{-1})

n=2	774.058							
n=3	3088.993	2846.495	2449.719	2443.500	2440.189	2319.058	2215.126	2090.697
	1990.429	1920.150	1909.535	1807.367	1680.964	1599.793	1579.359	1578.813
	1577.390	1489.258	1275.125	1099.854	944.679			
n=4	4097.150	4082.620	3873.222	3853.713	3633.127	3476.023	3468.264	3462.928
	3458.116	3411.629	3351.604	3343.735	3333.687	3240.262	3233.533	3229.815
	3109.090	3008.558	2945.283	2934.648	2884.130	2838.738	2836.739	2832.567
	2830.527	2829.199	2827.224	2787.228	2716.908	2712.270	2706.295	2706.110
	2624.924	2604.126	2603.943	2520.595	2477.722	2444.796	2432.932	2396.553
	2379.427	2377.458	2375.573	2306.477	2302.174	2292.589	2257.637	2195.687
	2192.434	2168.875	2164.824	2131.252	2086.635	2078.458	1976.028	1967.680
	1941.916	1910.947	1903.186	1896.622	1845.473	1748.012	1663.632	1651.223
	1634.084	1581.540	1448.531	1385.549				

Table IV. The calculated energy levels in Fit B for other F_2 states without observed data (in cm^{-1})

N=2	778.309						
N=3	1496.547	1279.868	1102.618	945.771			
N=4	2177.309	1925.826	1918.702	1911.620	1855.411	1809.079	1682.927	1669.183
	1655.980	1644.807	1600.570	1588.721	1578.839	1575.762	1569.344	1451.455
	1388.306						
N=5	3092.260	2722.565	2649.070	2592.144	2526.968	2462.997	2455.394	2447.251
	2436.558	2430.680	2421.387	2322.520	2318.279	2310.335	2305.182	2296.747
	2272.404	2257.953	2228.585	2218.677	2216.229	2195.354	2193.315	2173.913
	2157.729	2132.698	2102.615	2092.409	2089.835	2080.143	2073.023	2039.092
	1990.464	1976.180	1963.068	1956.843	1938.327	1906.334	1897.406	1848.606
	1824.641	1748.271	1655.093				
N=6	4078.063	3543.827	3517.840	3426.476	3261.511	3258.607	3217.764	3207.488
	3203.984	3090.515	3082.210	3046.639	2992.877	2977.422	2955.982	2952.235
	2946.590	2941.518	2939.587	2928.298	2903.491	2901.129	2894.450	2886.484
	2853.321	2846.446	2841.328	2838.193	2835.863	2835.647	2832.926	2831.058
	2828.552	2806.848	2793.846	2789.674	2760.970	2742.810	2741.421	2725.766
	2719.000	2715.320	2714.351	2708.920	2701.105	2698.761	2693.801	2685.015
	2678.378	2672.708	2660.143	2655.004	2647.133	2638.670	2630.250	2615.894
	2607.824	2598.092	2585.833	2582.730	2555.568	2535.720	2505.022	2487.403
	2480.529	2477.413	2470.023	2468.413	2454.484	2444.678	2425.891	2414.598
	2409.308	2398.143	2383.593	2380.054	2373.934	2363.527	2341.447	2321.627
	2311.420	2307.632	2297.550	2241.223	2226.891	2190.736	2144.527	

Table V. Obtained parameters for infrared transition intensities of SiF$_4$

	γ_s	γ_b	γ_{sb}	η_s	η_b	SD
Fit A	39.276	21.642	61.850	3.578	3.281	1.745
Fit B	37.472	21.441	61.944	3.527	3.285	2.015